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Nuclear-magnetic-resonance measurements of the hydrogen dynamics in nanocrystalline graphite

E. Stanik and G. Majer[a)]
Max-Planck-Institut für Metallforschung, Heisenbergstraße 3, 70569 Stuttgart, Germany

S. Orimo
Institute for Materials Research, Tohoku University, Sendai 980-8577, Japan

T. Ichikawa and H. Fujii
Natural Science Center for Basic Research and Development, Hiroshima University, Higashi-Hiroshima 739-8526, Japan and Graduate School of Advanced Sciences of Matter, Hiroshima University, Higashi-Hiroshima 739-8530, Japan

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Hydrogen-loaded nanocrystalline graphite samples have been prepared by mechanical milling under a hydrogen atmosphere. Milling vials and balls made of agate and ZrO_2 have been used to prepare samples with hydrogen contents between 1 and 2 wt %. The proton nuclear-magnetic-resonance (^{1}H-NMR) spectra of these samples are well represented by the sum of a broad Gaussian and a more narrow Lorentzian line corresponding to hydrogen in C–H covalent bonds as well as to hydrogen in methyl groups. The temperature dependence of the Lorentzian line can be ascribed to a hindered rotation of the methyl groups. The corresponding activation enthalpy of about 0.12 eV has been deduced from the spin-lattice relaxation rates between 250 and 450 K. Below about 200 K the relaxation rates are temperature independent but they depend strongly on the NMR frequency and on the parameters of the sample preparation. The relaxation due to paramagnetic impurities as well as the cross relaxation of the proton spins with spins of quadrupolar impurity nuclei are proposed to contribute significantly to the measured spin-lattice relaxation rates. © *2005 American Institute of Physics*. [DOI: 10.1063/1.2006971]

I. INTRODUCTION

Carbon nanostructures came into the limelight as attractive candidates for hydrogen storage systems after reports about high hydrogen storage capacities appeared. The research activities in this field have grown tremendously since then (an overview is given in Ref. 1). Orimo *et al.* introduced a rather simple but effective way of producing nanostructured hydrogen-graphite systems.[2,3] By mechanical milling of graphite powder under a hydrogen atmosphere samples with up to 7 wt % of hydrogen can be obtained.[2,3] The maximum storage capacity is reached if Cr-steel vials and balls are used for the sample preparation. The catalytic effect of iron in nanocrystalline graphite plays a crucial role for the hydrogen uptake.[4,5] However, the mechanisms of hydrogenation and the positions occupied by the hydrogen atoms are not yet well understood. The present paper reports on NMR measurements that have been performed in order to obtain information on the structural and dynamical properties of hydrogen in nanocrystalline graphite.

The nanocrystalline graphite samples have been characterized previously by several methods. X-ray diffraction (XRD) measurements have demonstrated that the destruction of the crystal structure is much more efficient for steel-milled samples than for those milled by agate or zirconium dioxide vials and balls. The XRD profile of an 80-h steel-milled sample has a broad shape, which indicates the destruction of the long-range order. After heating this sample to 1073 K the diffraction peak corresponding to the ordering of the interlayer of graphite reappears.[3] In the case of a 5-h agate-milled sample, the crystalline structure was hardly demolished, and no significant difference in the XRD spectra could be observed before and after heating the sample.[6] To investigate the hydrogen desorption properties of nanocrystalline graphite, thermal desorption spectroscopy (TDS) has been applied. The hydrogen desorption starts at about 600 K. A second desorption maximum at about 1000 K has been observed for the samples prepared with steel vials and balls.[4]

Neutron diffraction measurements have been performed on nanocrystalline graphite obtained by mechanical milling under deuterium atmosphere.[7] These measurements provide information on the positions occupied by the deuterium atoms. Considering the peaks in the radial distribution function, there are at least two different types of deuterium atoms in these samples: one fraction of deuterium atoms occurs in single C–D covalent bonds at the edges of the graphene planes. Another fraction is characterized by a distance of 0.18 nm to neighboring atoms. Such a distance can be found in methyl groups, where neighboring hydrogen atoms are 0.179 nm apart. According to Itoh *et al.*,[7] neutron-scattering data show that sp^3-hybridized carbon is formed in nanocrystalline graphite systems prepared by mechanical milling under a hydrogen/deuterium atmosphere.

Our first NMR measurements on nanocrystalline hydrogen-graphite systems have been published previously.[8,9] These first results show that the proton NMR

[a)]Electronic mail: majer@mf.mpg.de

TABLE I. Nanocrystalline graphite samples for the NMR measurements.

Sample	Hydrogen content	Impurities
*n*CH (agate, 5 h)	1.4 wt % (±0.3 wt %)	ca. 6.5 wt %
*n*CH (agate, 80 h)	1.4 wt % (±0.1 wt %)	ca. 9.0 wt %
*n*CH (agate, 200 h)	2.0 wt % (±0.1 wt %)	ca. 9.8 wt %
*n*CH (ZrO_2, 32 h)	<2.3 wt %	<6.6 wt %
*n*CH (ZrO_2, 80 h)	2.3 wt % (±0.2 wt %)	ca. 6.6 wt %

spectra of the nanocrystalline hydrogen-graphite samples (nCH_x) are well represented by the sum of a broad Gaussian and a more narrow Lorentzian line, indicating at least two different types of hydrogen coordinations. The temperature dependence of the spin-lattice relaxation rates could be fitted by a BPP curve with an activation enthalpy of about 0.1 eV. This low activation enthalpy suggests a high hydrogen mobility already at temperatures slightly above room temperature. In the present paper a more detailed proton NMR study on a variety of different nanocrystalline graphite samples is presented. The main aims of the study are to obtain information on the sites occupied by hydrogen and on the atomistic mechanisms of the hydrogen dynamics in these systems. During the process of mechanical milling of graphite, impurities from the milling vial and balls may enter the sample. The effects of these impurities on the NMR data, particularly on the spin-lattice relaxation rates, are investigated as well.

II. EXPERIMENT

A. Preparation of the samples

The nCH_x samples were prepared by mechanical milling under hydrogen atmosphere using a planetary ball mill apparatus (Fritsch P7) at 400 rpm. A major concern in this technique is that impurities from the milling atmosphere (mainly nitrogen and oxygen) or from the milling vial and balls may enter the sample during the milling process.[10] Milling vials and balls made of either agate or zirconium dioxide (ZrO_2) were used to prepare the samples for the present NMR studies. The milling atmosphere consisted of high-purity hydrogen (99.9999% purity) of 1 MPa initial pressure for the ZrO_2 milling vials and 0.3 MPa for the agate milling vials. Milling times between 5 and 200 h were chosen, resulting in hydrogen concentrations between 1 and 2 wt %. The hydrogen contents and the levels of impurities have been determined by oxygen combustion analysis. Table I gives an overview of the samples studied in the present work.

With stainless steel vials and balls a maximum hydrogen content of about 7 wt % can be reached, which corresponds to almost one hydrogen atom per carbon atom. However, contaminations from the milling vials and balls affect the NMR measurements. In the case of long milling times with stainless steel vials and balls, the iron impurities in the nanocrystalline graphite may be of such an extent that NMR measurements on these samples cannot be carried out because of the magnetic properties of the sample.

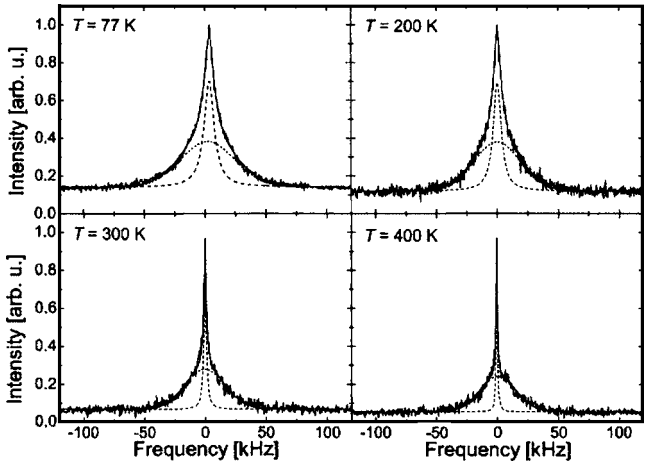

FIG. 1. ^{1}H-NMR spectra of *n*CH (ZrO_2,32 h) at different temperatures between 77 and 400 K. Dashed and dotted lines are Lorentzian and Gaussian curves, respectively. The solid lines represent the sum of both.

B. NMR measurements

The NMR measurements were carried out at 32.6 and 67.7 MHz using a home-built computer-controlled NMR spectrometer with phase-alternating pulse schemes and quadrature detection. The spectra were obtained by Fourier transformation of the free-induction decay following a single 90° pulse after a dead time of 10 μs. Typically, a total of 32 to 200 shots were added to obtain the final spectra. The spin-lattice relaxation rates were measured by using an inversion-recovery pulse sequence ($180°-\tau-90°$) and varying the waiting time τ. In the case of *n*CH (agate, 80 h) NMR measurements were also performed at 311 MHz using a Bruker MSL 300 spectrometer.

III. RESULTS AND DISCUSSION

A. ^{1}H-NMR spectra

The ^{1}H-NMR spectra of nanocrystalline graphite samples consist generally of two lines: a broad Gaussian line and a more narrow Lorentzian line. Typical examples of the ^{1}H-NMR spectra are shown in Fig. 1. The corresponding values of the linewidths are summarized in Table II. The observed spectra depend on the structural and dynamical properties of hydrogen in nCH_x. The dipole-dipole interaction between the nuclei results in a distribution of local magnetic fields and thus in a line broadening at low temperatures. Hydrogen motion causes fluctuations of these local fields. If the characteristic rate of hydrogen motion is greater than the

TABLE II. Linewidths at different temperatures measured on *n*CH (ZrO_2, 32 h) at 32.6 MHz.

Temperature (K)	Linewidth of Lorentzian line (kHz)	Linewidth of Gaussian line (kHz)
77	10.1	45
200	7.9	38
300	2.8	33
400	1.4	30
516	0.7	25

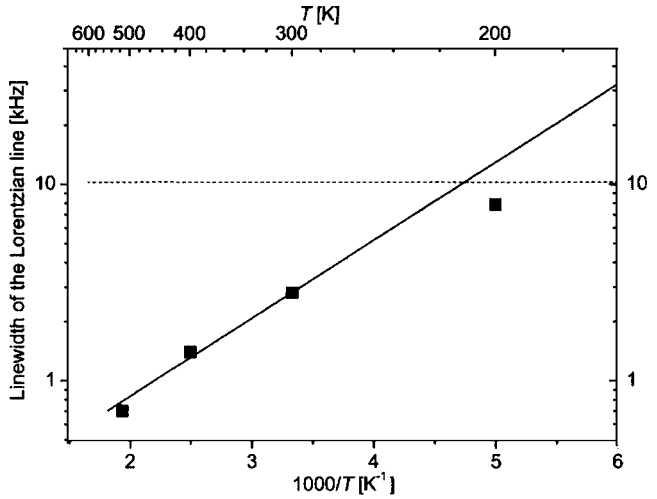

FIG. 2. Linewidth of the Lorentzian curve in the ^{1}H-NMR spectrum of *n*CH (ZrO_2,32 h) plotted against the inverse sample temperature. The solid line corresponds to an activation enthalpy of about 0.1 eV for the motion that is responsible for the motional line narrowing. The dashed line represents the "rigid lattice" value of the linewidth measured at 77 K.

NMR linewidth at low temperatures, a motional narrowing of the NMR line occurs. In this motional narrowing regime the inverse linewidth is expected to be proportional to the rate of hydrogen motion. In the case of the Lorentzian line, the linewidth is about 10 kHz at 77 K, and above about 200 K it decreases strongly with increasing temperature. This indicates a thermally activated motion of the corresponding hydrogen atoms. Figure 2 shows the temperature dependence of the linewidth of the Lorentzian line on a logarithmic scale. The slope of the solid line in this figure corresponds to an activation enthalpy of about 0.1 eV. The temperature dependence of the Gaussian line is much less pronounced, indicating a lower mobility of the respective protons.

The composition of the NMR spectra leads to the conclusion that the samples contain hydrogen atoms in at least two different configurations. This is in good agreement with the results of the neutron diffraction measurements.[7] It is reasonable to assume that a certain amount of the hydrogen atoms forms single C–H bonds: the graphitic planes break during the milling process and many dangling bonds are created at the edges of the graphene platelets. Electron-spin-resonance (ESR) measurements have been performed on some of the samples. The ESR spectra are not shown, but they confirm the presence of dangling bonds in the ball-milled graphite. Hydrogen atoms partially saturate these dangling carbon bonds forming C–H covalent bonds. The dynamics of this fraction of hydrogen is strongly reduced and no motion-induced phenomena are expected in the NMR data. For this reason the hydrogen atoms in the C–H bonds are ascribed to the Gaussian line in the ^{1}H-NMR spectra.

The Lorentzian line, on the other hand, is due to a more mobile fraction of the hydrogen atoms. As suggested in a previous analysis of our first proton NMR studies on nanocrystalline graphite,[9] the Lorentzian line may be ascribed to hydrogen in graphite interlayers. This seems to be reasonable as the activation enthalpy of the motion is in the range of the van der Waals binding energy of hydrogen on a graphene sheet. However, considering the high hydrogen desorption temperatures further assumptions regarding the hydrogen release at the edges of the crystalline grains would be required in this model. A much more straightforward explanation is to assume a localized motion of the hydrogen atoms. These assumptions are in excellent agreement with the results of neutron-scattering measurements,[7] which give strong evidence of the formation of sp^3-hybridized carbon atoms in the nanocrystalline graphite prepared by milling under a deuterium atmosphere. The more mobile fraction of the hydrogen atoms can then be understood quite naturally as due to the formation of methyl groups. The hindered rotation of the methyl groups explains the partial motional narrowing of the Lorentzian NMR line. This methyl-group rotation is a strictly localized motion, which is consistent with the high desorption temperatures of hydrogen from the ball-milled graphite samples. An activation enthalpy of about 0.1 eV, as deduced from the slope of the solid line in Fig. 2, is a reasonable value for a methyl-group rotation.[11,12] The relative intensities of the two lines in the ^{1}H-NMR spectra are a measure of the fractions of hydrogen atoms in the respective components. Figure 3 shows a comparison of spectra measured on samples that have been prepared with different milling vials and balls and different milling times. In the same figure a bar graph is included, which shows the relative area of the Lorentzian and Gaussian part of the spectra. For *n*CH (agate, 5 h), a 5-h ball-milled sample prepared with agate milling tools, the Lorentzian line shows a higher relative intensity than in all other samples. Due to the short milling time and the low density of the agate balls, the deformation of the graphite powder is less pronounced in this sample. This leads to the conclusion that a significant fraction of hydrogen atoms forms CH_3 groups at the beginning of the milling process. Later, during the ongoing destruction of the graphite crystalline structure, hydrogen atoms are increasingly trapped by dangling bonds to form single C–H bonds. For a more precise quantitative analysis of the fractions of hydrogen atoms one has to take into account that the NMR signal is already reduced when the data acquisition starts after the dead time of the NMR probe. The signal reduction is not exactly known, and it is different for the two components of the NMR spectrum. This introduces an uncertainty in the data analysis but, for any reasonable assumption about the decay of the nuclear magnetization, the qualitative conclusions given above are correct.

B. Spin-lattice relaxation measurements

Further information on the nanocrystalline graphite samples is obtained by the measurements of the spin-lattice relaxation rates. The magnetization recovery in an inversion-recovery experiment could be reasonably well described by a single-exponential term. It was not possible to determine different Γ_1 values for the different components of the NMR spectra. This indicates an exchange of hydrogen atoms between the single C–H bonds and the CH_3 groups on the time

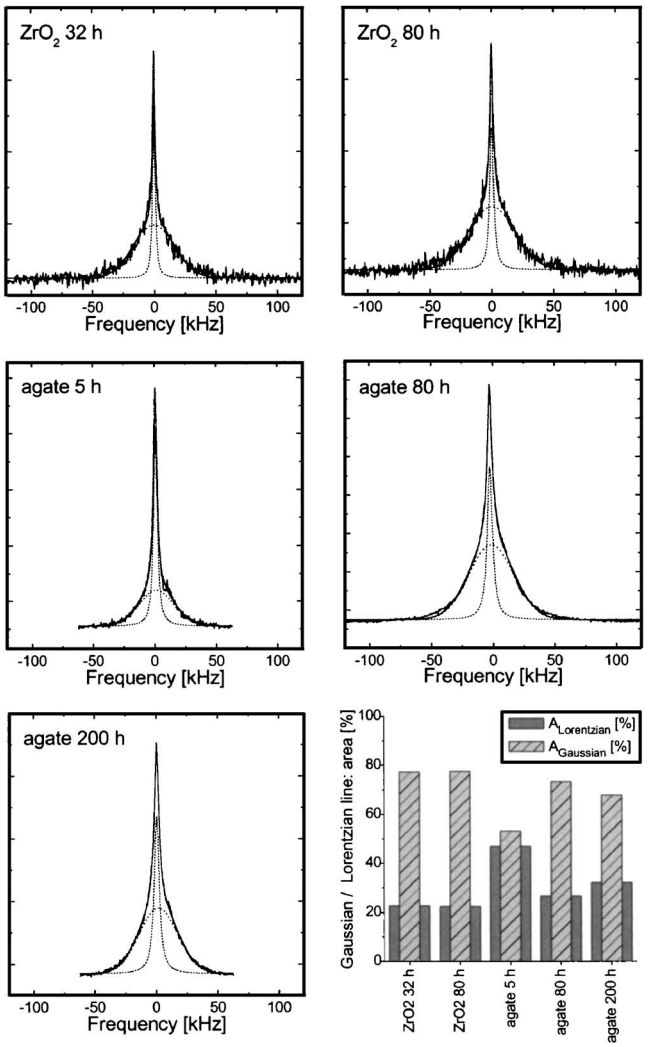

FIG. 3. Room-temperature spectra of nanocrystalline graphite samples prepared by mechanical milling under a hydrogen atmosphere with different milling times and different materials of the milling vials and balls. The bars on the lower right side indicate the relative areas of the Lorentzian curves (dark grey bars) and the Gaussian curves (dashed bars) in the different spectra.

scale of the Γ_1 measurements. The temperature-dependent Γ_1 data measured at different frequencies and on different samples are shown in Figs. 4–6.

For ^{1}H-NMR on hydrogen in solids three main contributions to the spin-lattice relaxation rate should be considered:[13] the dipolar relaxation $\Gamma_{1,d}$, the paramagnetic relaxation $\Gamma_{1,p}$, and the electronic relaxation $\Gamma_{1,e}$.

The dipolar relaxation rate is due to the magnetic dipole-dipole interaction of a given proton with neighboring protons and in general also with other nuclei. Owing to the low abundance of ^{13}C in natural graphite and the relatively small gyromagnetic ratio of this nucleus, the dipolar interaction with the carbon nuclei is expected to be negligible. However, the dipole-dipole interaction between protons and impurity nuclei may play a major role, and it may particularly contribute to cross-relaxation processes between these two spin systems (see below). The simplest approximation in order to obtain dynamical parameters is to analyze $\Gamma_{1,d}$ in terms of correlation functions that decay exponentially with time, as originally proposed for liquids by Bloembergen *et al.* (BPP model).[14] The corresponding spectral densities are simple Lorentzian functions. In the case of pure proton-proton interaction

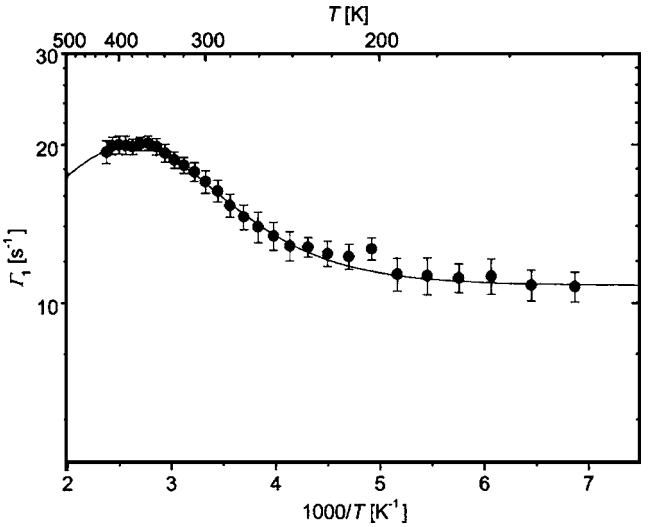

FIG. 4. Spin-lattice relaxation rates of *n*CH (agate, 80 h) at 67.7 MHz. The solid line represents the sum of a BPP fit and a temperature-independent contribution to the relaxation rate (offset).

$$\Gamma_{1,d} = \frac{2}{3} M_2 \left[\frac{\tau_c}{1+\omega_0^2 \tau_c^2} + \frac{4\tau_c}{1+4\omega_0^2 \tau_c^2} \right] \tag{1}$$

is obtained, where $\omega_0/2\pi$ is the resonance frequency and M_2 is the second moment in frequency units. The characteristic time for the change in the dipole-dipole interaction, the correlation time τ_c, is closely related to the mean time of residence of the mobile hydrogen atoms. For a thermally activated process of hydrogen motion, τ_c is given by

$$\tau_c = \tau_0 \cdot e^{H_a/k_B T}, \tag{2}$$

with the activation enthalpy for hydrogen motion H_a. The maximum in $\Gamma_{1,d}$ is observed if τ_c is close to the inverse of the spin precession frequency.

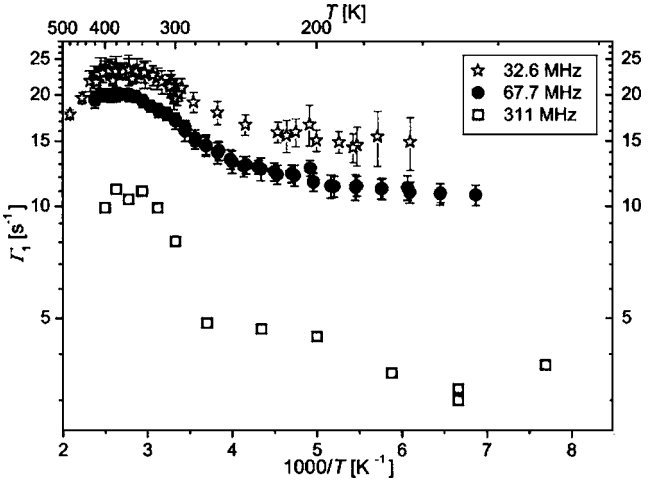

FIG. 5. Spin-lattice relaxation rate of protons in *n*CH (agate, 80 h) measured at three NMR resonance frequencies (32.6, 67.7, and 311 MHz).

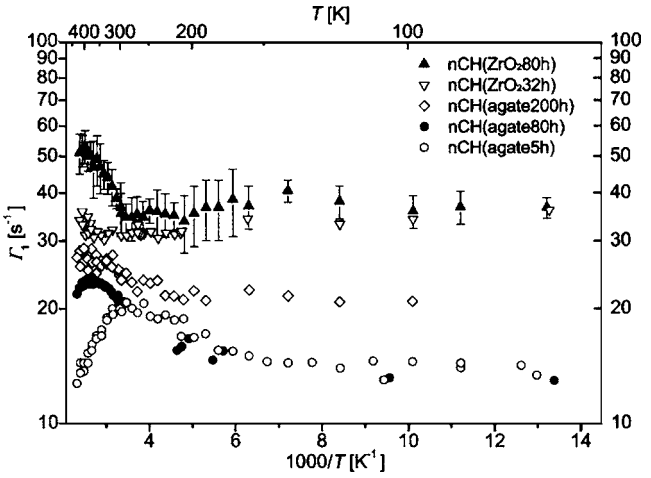

FIG. 6. The spin-lattice relaxation rates of different nanocrystalline graphite samples measured at 32.6 MHz. The error bars all have similar sizes and were, for clarity, removed except for one set of data.

In Fig. 4 the relaxation rates of *n*CH (agate, 80 h) are shown for a temperature range from 150 to 430 K. At about 380 K the maximum relaxation rate has been observed. The solid line represents the fit of a BPP curve [Eq. (1)] plus a temperature-independent offset. The relaxation mechanisms related to the offset will be discussed below. The BPP fit yields an activation enthalpy of 0.12 eV. This is a reasonable value for the methyl-group rotation in the nanocrystalline graphite sample. Similar activation enthalpies have been found earlier for the rotation of methyl groups in solids.[11,12]

Although the temperature dependence of $\Gamma_{1,d}$ is well represented by a BPP formula (see Fig. 4), the mechanisms of the dipolar relaxation are certainly more complex than a simple dipole-dipole interaction between neighboring protons. As already mentioned before, the BPP model predicts a relaxation maximum if the mean time of residence of the spin carriers is close to the inverse of the spin precession frequency. Thus, for a thermally activated process of hydrogen motion, the temperature of the relaxation maximum is expected to be higher the higher the resonance frequencies. However, as it is evident from Fig. 5, the relaxation rate reveals essentially no frequency dependence of the position of the relaxation maximum. For all three frequencies (32.6, 67.7, and 311 MHz), the proton relaxation maximum is observed at about 380 K. This frequency independence of the relaxation maximum is quite unusual even if one takes into account that strong paramagnetic relaxation effects contribute to the spin-lattice relaxation. The paramagnetic relaxation $\Gamma_{1,p}$ is due to the dipole-dipole interaction between the magnetic moments of protons and of unpaired electron spins at paramagnetic centers. The paramagnetic centers in the samples may be due to both impurities and dangling bonds produced in the graphite by the ball-milling treatment. The ESR spectra revealed only a broad free-electron signal, and it was not possible to identify any particular paramagnetic ions. Nevertheless, a frequency dependence of the position of the relaxation maximum is also expected for the paramagnetic relaxation, independent of the kind of the paramagnetic centers interacting with the protons.[15]

The observed frequency independence of the position of the relaxation maximum cannot be explained easily. We suggest to interpret these results in terms of a strong cross relaxation of the proton spins with spins of quadrupolar nuclei of impurities.[13] Lichty *et al.* have demonstrated that cross relaxation between proton and quadrupolar nuclear spins can contribute significantly to the spin-lattice relaxation in metal-hydrogen systems.[16] We expect this cross relaxation to be very pronounced if the rotation frequency of the methyl groups happens to equal some combined Zeeman-quadrupolar splitting of the impurity nuclei. The impurity spins in turn transfer the magnetization to the lattice via their own fast relaxation rate. For quadrupolar nuclei the level splitting is often dominated by the quadrupolar interaction with electric-field gradients and thus almost independent of the applied magnetic field. The applied magnetic field, on the other hand, determines the resonance frequency of the protons. The agate milling tools consist mainly of SiO_2, but they also contain small amounts of several metal oxides, for example, MnO and MgO. The quadrupolar moments of ^{55}Mn and ^{25}Mg (about 10% natural abundance) are 0.55 and 0.22 b, respectively.[17] As indicated in Table I, the samples contain several wt % of impurities, which have been introduced during the milling process. X-ray diffraction studies on similar materials give evidence that the impurities are not in separate phases and hence can possibly lead to large cross relaxation between protons and the various quadrupolar nuclei that are in the vicinity.

The relaxation model suggested above is consistent with our experimental results, and we are not aware of any other model that provides a reasonable explanation of the unusual frequency independence of the position of the relaxation maximum. We like to emphasize that this model implies the assumption of a rather strong interaction between the quadrupolar impurity nuclei and the protons at the methyl groups. A final proof of the correctness of this model is not possible on the basis of the present data.

The electronic relaxation $\Gamma_{1,e}$ accounts for the dipolar interactions with magnetic moments of conduction electrons. In metallic hydrides the electronic relaxation $\Gamma_{1,e}$ is given by the Korringa law[18]

$$\Gamma_{1,e} = K_e \cdot T, \tag{3}$$

where K_e depends on the density of states at the Fermi energy. In the case of hydrogen in nanocrystalline graphite, no linear increase of Γ_1 with increasing temperature has been observed over the entire temperature range between 200 and 500 K. This indicates that the electronic contribution $\Gamma_{1,e}$ is negligible, which is in good agreement with the relatively low electric conductivity of the nanocrystalline graphite.

In the following discussion we address the relaxation behavior at temperatures well below the relaxation maximum. A possible explanation of the experimental data would be that the cross relaxation with quadrupolar impurity nuclei discussed above also provides a major contribution to the relaxation rates at low temperatures.[16] In metal-hydrogen systems, the cross relaxation between protons and quadrupolar nuclear spins was found to increase with decreasing proton resonance frequency.[16] A similar frequency dependence

has been found for the relaxation rates of protons in *n*CH (agate, 80 h). On the other hand, the paramagnetic relaxation $\Gamma_{1,p}$ may also play an important role for the relaxation at low temperatures where the motional excitations of the hydrogen atoms are frozen. Similar to the cross-relaxation with quadrupolar nuclei, the paramagnetic relaxation strength increases with decreasing NMR frequency.[15] A comparison of different nanocrystalline graphite samples shows that the low-temperature relaxation rates depend on both the material and the milling time used for the sample preparation. For a given material of the vial and balls, longer milling times result in higher spin-lattice relaxation rates (see Fig. 6). As the fraction of paramagnetic impurities is expected to increase with increasing milling time, $\Gamma_{1,d}$ seems to contribute significantly to the relaxation rates measured at low temperatures.

IV. SUMMARY

^{1}H-NMR measurements have been performed on nanocrystalline hydrogen graphite systems prepared by mechanical milling under hydrogen atmosphere. The NMR spectra are well described by the sum of a Lorentzian and a Gaussian line. These two lines can be ascribed to hydrogen in methyl groups as well as to hydrogen in single covalent C–H bonds at the edges of graphene planes. A pronounced decrease in the linewidth with increasing temperature has been observed for the Lorentzian line. This is most likely due to a motional narrowing caused by the rotation of the methyl groups. From the temperature dependence of the linewidth an activation enthalpy of about 0.1 eV is obtained for the methyl-group rotation.

Spin-lattice relaxation rates have been measured over wide temperature ranges on several nanocrystalline graphite samples. Fitting the sum of a BPP function and a constant offset to the relaxation data of *n*CH (agate, 80 h) yields an activation enthalpy of 0.12 eV for the methyl-group rotation. Γ_1 measurements performed at 32.6, 67.7, and 311 MHz indicate that the offset depends strongly on the NMR frequency, whereas the position of the relaxation maximum is about the same for all frequencies. A possible explanation for this unusual behavior of the relaxation maximum is a cross relaxation between protons and quadrupolar nuclei. The constant offset, which dominates the relaxation rate at low temperatures, depends not just on the NMR frequency but also on the parameters of the sample preparation, particularly on the material of the milling tools. We suggest that this contribution to the spin-lattice relaxation is mainly due to paramagnetic impurities although a contribution from cross relaxation with quadrupolar nuclei may also be involved. A Korringa-like electronic relaxation can be excluded.

ACKNOWLEDGMENTS

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[1] L. Schlapbach and A. Züttel, Nature (London) **414**, 353 (2001).
[2] S. Orimo, G. Majer, T. Fukunaga, A. Züttel, L. Schlapbach, and H. Fujii, Appl. Phys. Lett. **75**, 3093 (1999).
[3] S. Orimo, T. Matsushima, H. Fujii, T. Fukunaga, and G. Majer, J. Appl. Phys. **90**, 1545 (2001).
[4] S. Isobe, T. Ichikawa, J. Gottwald, E. Gomibuchi, and H. Fujii, J. Phys. Chem. Solids **65**, 535 (2004).
[5] T. Kiyobayashi, K. Komiyama, N. Takeichi, H. Tanaka, H. Senoh, H. T. Takeshita, and N. Kuriyama, Mater. Sci. Eng., B **108**, 134 (2004).
[6] T. Ichikawa (unpublished).
[7] K. Itoh, Y. Miyahar, S. Orimo, H. Fujii, T. Kamiyama, and T. Fukunaga, J. Alloys Compd. **356–357**, 608 (2003).
[8] G. Majer, U. Eberle, F. Kimmerle, E. Stanik, and S. Orimo, Physica B **328**, 81 (2003).
[9] G. Majer, E. Stanik, and S. Orimo, J. Alloys Compd. **356–357**, 617 (2003); **377**, 316(E) (2004).
[10] C. Suryanarayana, Prog. Mater. Sci. **46**, 1 (2001).
[11] K. Grude, J. Haupt, and W. Müller-Warmuth, Z. Naturforsch. A **21a**, 1231 (1966).
[12] B. Black, G. Majer, and A. Pines, Chem. Phys. Lett. **201**, 550 (1993).
[13] R. G. Barnes, *Hydrogen in Metals III*, edited by H. Wipf (Springer, Berlin, 1997), p. 93.
[14] N. Bloembergen, E. M. Purcell, and R. V. Pound, Phys. Rev. **73**, 679 (1948).
[15] T.-T. Phua, B. J. Beaudry, D. T. Peterson, D. R. Torgeson, R. G. Barnes, M. Belhoul, G. A. Styles, and E. F. W. Seymour, Phys. Rev. B **28**, 6227 (1983).
[16] L. R. Lichty, J.-W. Han, D. R. Torgeson, R. G. Barnes, and E. F. W. Seymour, Phys. Rev. B **42**, 7734 (1990).
[17] P. P. Man, http://www.pascal-man.com/periodic-table/periodictable.html
[18] J. Korringa, Physica (Amsterdam) **16**, 601 (1950).